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SYNTHESIS OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS INCLUDING A --ETC(U)

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STUDIES OF SILICON-NITROGEN-PHOSPHORUS
COMPOUNDS INCLUDING A NEW
SYNTHESIS OF PHOSPHAZENES

Final Report

by

Robert H. Neilson

March 26, 1979

U.S. ARMY RESEARCH OFFICE
grant number: DAAG29-77-G-0214

Duke University
Durham, North Carolina 27706

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phosphazenes silylaminophosphine silicon-nitrogen-phosphorus		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The research under ARO sponsorship has been directed toward the synthesis, characterization, structural isomerization, and thermal decomposition reactions of new silicon-nitrogen-phosphorus compounds. Some of these compounds undergo smooth decomposition when heated to afford phosphazenes, oligomeric materials of general formula (NPRR') _n . Other types of Si-N-P compounds readily isomerize (usually irreversibly) via 1,3-silyl shifts to give new phosphine imines, compounds possessing the -N=P< functionality.		

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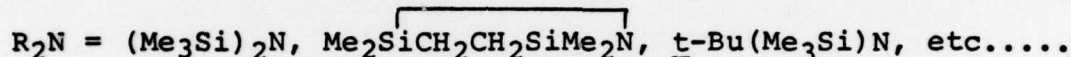
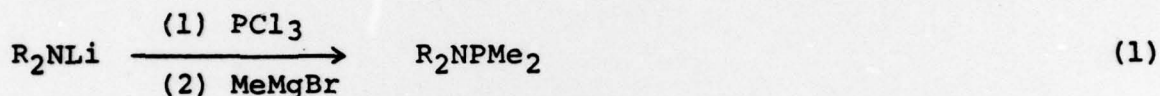
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SUMMARY OF RESEARCH FINDINGS

During the period covered by this report, our research has progressed in two separate but related areas.

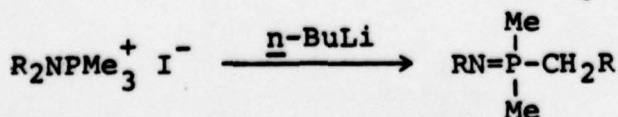
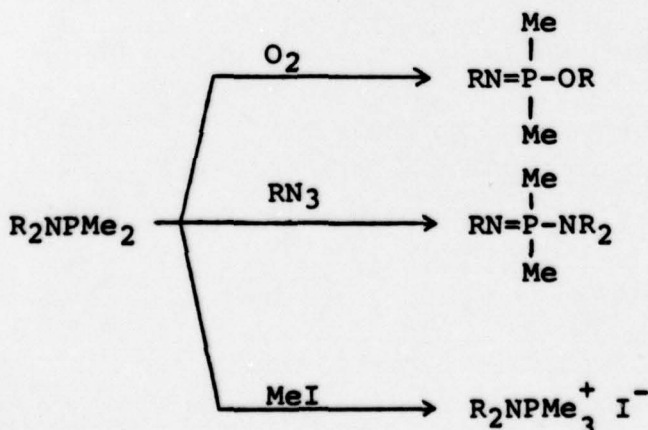
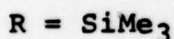
(1) Synthesis and Isomerization of Si-N-P Compounds

We have developed¹ a convenient, "one-pot" synthesis of silylamino-phosphines (eq. 1) containing alkyl groups (e.g. Me) on phosphorus. This method affords high yields, allows the use of large quantities of reactants,



permits a variety of substituent combinations, and avoids the use of reagents like Me_2PCl which are difficult to prepare and manipulate.

These silylamino-phosphines readily undergo a variety of oxidation reactions with reagents such as O_2 , Me_3SiN_3 and MeI yielding new silylamino-phosphine oxides², imines,³ and phosphonium salts¹, respectively. Treatment of the phosphonium salts with $n\text{-BuLi}$ causes dehydrohalogenation and subsequent isomerization to new (silylmethyl)phosphine imines.¹ These reactions are illustrated in equations 2 and 3 where, for simplicity, only the $(\text{Me}_3\text{Si})_2\text{N}$ substituent is shown. Similar reactions occur for compounds containing a variety of other silyl groups as described in the publications cited.

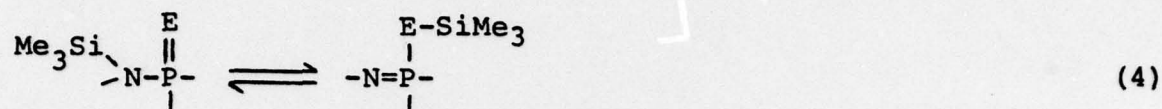


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These four-coordinate Si-N-P compounds often undergo structural isomerization via 1,3-silyl shifts (eq. 4) from which the products are novel phosphine imines. This process is irreversible for most oxides ($E = O$)²

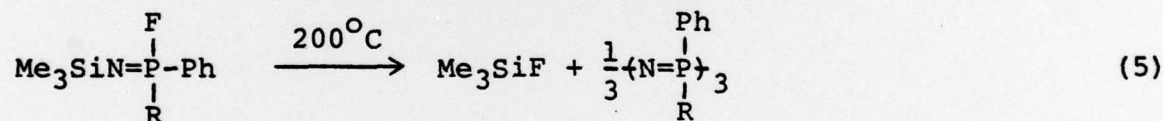


and ylides ($E = \text{CR}_2$)¹ but can, in some cases, be reversible (on the NMR time scale) for imines ($E = \text{NR}$).³

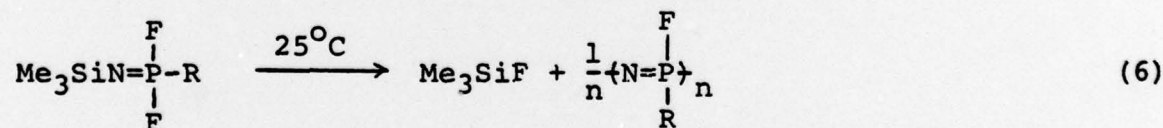
We have also prepared⁴ a series of Si-N-P compounds which contain P-halogen substituents and are stabilized by the *t*-BuMe₂Si substituent. These include the first stable acyclic silylaminophosphorane, *t*-BuMe₂SiN(Me)PF₄, and the first stable N-silyl-P-trihalophosphine imine, *t*-BuMe₂SiN=PCl₃. Steric crowding at silicon enhances the thermal stability of these compounds relative to their Me₃Si analogues which readily eliminate Me₃SiX.

(2) Synthesis of Phosphazenes from Si-N-P Compounds

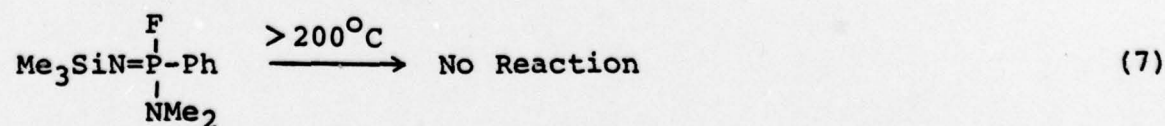
The thermal decomposition of suitably constructed N-silylphosphine imines continues to be studied in our laboratory as a useful synthetic route to phosphazenes. We have found that some reactions proceed smoothly to give good yields of the cyclic trimers (eq. 5) while other reactions (eq. 6) afford mixtures of oligomers having, as yet undetermined, molecular weights. Interestingly, the phenyl(dimethylamino) derivative (eq. 7) has, under the same conditions, resisted decomposition.



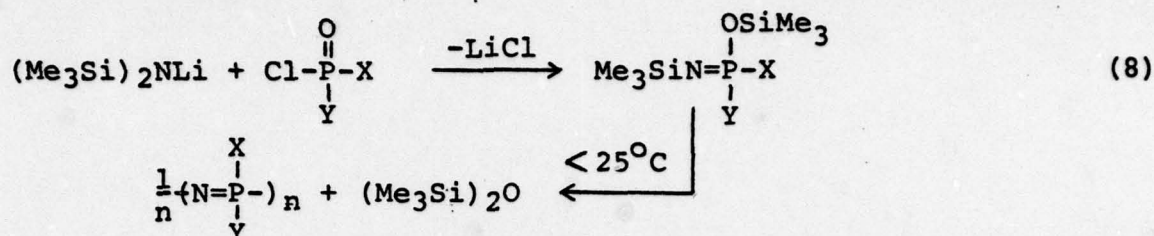
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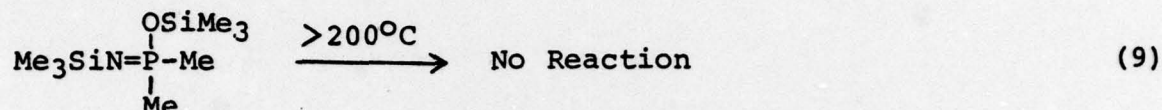
R = Me, NMe₂



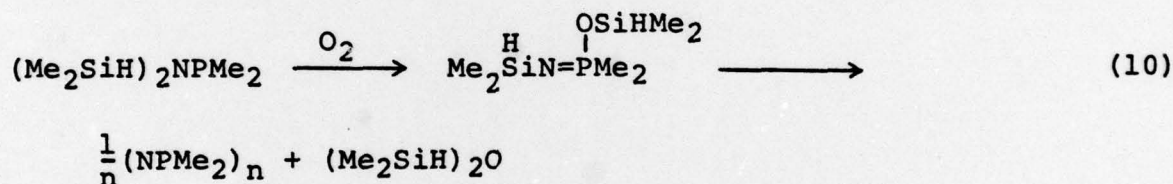
In a somewhat different approach, we have studied the possibility of thermal elimination of (Me₃Si)₂O from several disilylated phosphine imines (eqs. 8 and 9). The compounds⁵ prepared according to eq. 8, however, were



X = Ph	Ph	Cl
Y = Cl	NMe ₂	NMe ₂



not acceptable as phosphazene precursors because their instability prevented their isolation as pure materials. The success of reactions such as eq. 9 may well be dependent upon the use of smaller silyl groups. Preliminary experiments (eq. 10) have shown that this is indeed the case and that dimethylphosphazenes can be produced by this method.



PUBLICATIONS

- (1) J. C. Wilburn and R. H. Neilson, "Synthesis of (Silylmethyl)phosphinimines via Silyl Migration from Nitrogen to Carbon," Inorg. Chem., **18**, 347 (1979).
- (2) R. H. Neilson, R. D. Jacobs, R. W. Scheirman, and J. C. Wilburn, "Structural Isomerization of Bis(trimethylsilyl)aminophosphine Oxides," Inorg. Chem., **17**, 1882 (1978).
- (3) J. C. Wilburn, P. Wisian-Neilson, and R. H. Neilson, "Synthesis and Structural Isomerism of Some Silylaminophosphinimines," Inorg. Chem., in press.
- (4) R. H. Neilson and W. A. Kusterbeck, "Synthesis of Silicon-Nitrogen-Phosphorus Halides Stabilized by the tert-Butyldimethylsilyl Group," J. Organometal. Chem., **166**, 309 (1979).
- (5) J. Butvinik and R. H. Neilson, "Reactions of Lithium Bis(trimethylsilyl)amide with Some Phosphoryl Chlorides," Inorg. Nucl. Chem. Lett., **14**, 497 (1978).
- (6) J. C. Wilburn, Ph.D. Dissertation, Duke University, 1978.